

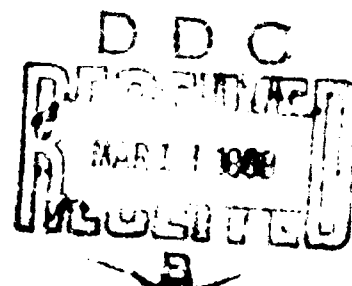
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ON THE EQUATION OF STATE OF COMPRESSED
LIQUIDS AND SOLIDS

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ON THE EQUATION OF STATE OF
COMPRESSED LIQUIDS AND SOLIDS

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ABSTRACT: Since the work of van der Waals on gases and Mie and Grüneisen on solids which produce an equation of state of the form

$$p = G(v,T) NkT/v + p_0(v) ,$$

many theoretical equations of state have been developed which can be put into the above form. Despite this fact it has been almost a universal fad to describe equations of state through the dimensionless compressibility factor, $F(v,T) = pv/NkT$ instead. It is shown here that considerable useful information is discarded when the latter form is used. In particular an analysis of p_0 and $G(v,T)$ for the Lennard-Jones Devonshire free volume theory and the equation of state results obtained by the Monte Carlo method have shown that these approaches lead to essentially the Mie-Grüneisen equation at high density when the temperature is low enough. At higher temperatures for high density and for all temperatures at lower densities the two theories come close to the usual theories for dense fluids. In addition, the functional relations for $G(v,T)$ are sufficiently simple to be replaced by analytic functions to facilitate the application of the theories to practical problems. It should even be possible to empirically improve on the original theories by making the empirical equations conform to our best knowledge of the states, solid or fluid, being described. For illustration an analytic fit to the Monte Carlo result for a Lennard-Jones 6-12 potential is presented. A breakdown of Lennard-Jones result for the second virial coefficient is appended.

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ON THE EQUATION OF STATE OF COMPRESSED LIQUIDS AND SOLIDS

This report is an analysis of two classically important equations of state for molecular systems of non-ionic, non-metallic molecules. The immediate purpose of this analysis was to arrive at a better understanding of the equation of state problem for a simple fluid or solid so that a better equation of state can be formulated for the description of detonation parameters; pressure, temperature, density, velocities, isentropes, and composition for the detonation of condensed explosives. The results described, however, should have a much broader application. The analytic form of an equation of state use here or a similar treatment, depending on the model, makes it possible to critically examine many theoretical equations. This would assist the writer and the user in establishing the merits, range of validity, and defects of each theory.

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A related report which discusses this work with more emphasis on the problem of detonation parameters was presented by the author, at the 12th International Symposium on Combustion at Poitiers, France on 15 July 1968. It will be published in the proceedings which will probably be available in late 1969.

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By direction

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1. INTRODUCTION

Since the introduction of the virial expansion by H. Kammerlingh Onnes¹ for the compressibility factor $F(v,T) = pv/NkT$ of non-ideal gases it has been common practice to describe the behavior of equations of state by showing how the function $F(v,T)$ varied with volume and temperature. Though there may be merit in this description when the density is moderate, i.e., below the normal density of a liquid, it now appears that a more descriptive dimensionless factor is available for states ranging in density all the way from the ideal gas to compressed solids or liquids. The parameter is obtained by analogy to the treatment of solids and to the van der Waals equation. The equation of state of solids has been successfully treated by splitting the pressure into two dominant terms; one which is purely volume dependent and derivable from an average potential function and one which is largely thermal in nature related to the lattice vibrations in the solid. This approach leads to an equation of state attributed to Mie and Grüneisen² which for a monatomic solid may be written as

$$p = \gamma C_V T/v - dE_0/dv \quad (1)$$

for which the energy is assumed to be separable and given by

$$E = E_1(T) + E_0(v) \quad (2)$$

with $E_1(T) = \int C_V(T) dT$. The dimensionless coefficient γ , the Grüneisen parameter, is treated as a constant or a function of v only. For monatomic solids above the Debye temperature C_V is essentially a constant having the value $3Nk$, and hence the first term on the right of Eq. (1) could be written as

$$\gamma C_V T/v = GNk T/v \quad (3)$$

By substituting Eq. (3) into Eq. (1) with $G = G(v,T)$ one arrives at a very general equation of state which not only describes a solid state but also is of use in describing liquid and gaseous states, i.e.

$$p = G(v,T)NkT/v + p_0 \quad (4)$$

in which p_0 is an internal pressure term derived from $E_0(v)$. The compressibility factor for Eq. (4) is

$$F(v,T) = G(v,T) + p_0 v/NkT \quad (5)$$

In the case of compressed solids, p_0 is the dominant term for p . Consequently, it is far more useful to examine the behavior of G and p_0 independently rather than F . It is readily seen that Eq's. (4) and (5) are equally applicable to states of moderate density. In the limit for large volumes $p_0 \rightarrow 0$ and $G \rightarrow 1$ to give the ideal gas equation. Over the range from ideal gas to about that of a normal liquid, one might expect G to increase with decrease of volume in a way similar to the behavior of the van der Waals equation or typical virial equations such as the Boltzmann equation of state for a gas composed of hard or compressible spherical molecules. In the range

References may be found on page 6

of volume from the normal solid and below, on the other hand, the behavior of the normal solid is that G should decrease with decrease in volume. This leads us to expect that G should have a maximum value at volumes near that of the normal liquid state. Furthermore, unlike the compressibility factor G should fall below 1 only if attractive terms other than in p_0 are present. It thus appears that an examination of G rather than F would shed considerable light on (a) the compression and compressibility of very dense "gases" such as the explosion products in a detonation of a condensed explosive, (b) the states reached by shock compression of liquids, or solids, and (c) the transition from the liquid to the solid state.

The utility of Eq. (4) is further enhanced if we consider it in the light of a well-known thermodynamic relation

$$p + (\partial E / \partial v)_T = T(\partial p / \partial T)_v \quad (6)$$

If, in addition, Eq. (2) is generalized to

$$E = E_1(v, T) + E_0(v) \quad (7)$$

we find it useful to define three pressure terms:

- a. a volume dependent internal pressure, $p_0 = -dE_0/dv$,
- b. an internal pressure term which depends on both volume and temperature, $p_1 = -(\partial E_1 / \partial v)_T$, and
- c. a thermal pressure term, $p_T = T(\partial p / \partial T)_v$.

Eq. (6) then becomes

$$p = T(\partial p / \partial T)_v - dE_0/dv - (\partial E_1 / \partial v)_T = p_T + p_0 + p_1 \quad (8)$$

It is easy to see that p_1 arises from a volume dependence of C_v . By definition $C_v = (\partial E / \partial T)_v = (\partial E_1 / \partial T)_v$. Then $(\partial C_v / \partial v)_T = \partial^2 E_1 / \partial T \partial v = -\partial p_1 / \partial T$. Thus if C_v depends on v , p_1 will be a function of T and, therefore, non zero. If C_v is independent of v , p_1 must vanish. For Eq. (4) $p_T = GRT/v + RT^2(\partial G / \partial T)_v/v$ and $p_1 = -RT^2(\partial G / \partial T)_v/v$. Thus if G is a function of T , p_1 will be non-zero. This indicates that G will be a function of T if C_v is a function of v and conversely.

In the original Grüneisen expression, Eq. (1), γ , as applied to metals and inorganic solids is treated as a constant or as a function of v only. But also C_v is usually considered to be constant (the equation best applies above the Debye temperature). If C_v is volume dependent then γ may also have to be a function of T . In that case, Eq. (4) may be just as good a working basis as Eq. (1).

An examination of experimental data for the behavior of G in the liquid-solid regions of molecular materials is not easy. There are, however, two theoretical approaches which have been aimed to describe this density region for spherical molecules. Both are based on pairwise additivity of pair potentials for an extended system of molecules. They are the free volume equation of state exemplified by the treatment of Lennard-Jones Devonshire^{4,5}, LJD, and the Monte Carlo, MC, equation of state treatment^{6,7}. Both of these theoretical approaches confirm in a general way the expected behavior of $G(v, T)$. We there-

fore recommend the form of Eq. (4) in preference to the usual forms³ for $F(V,T)$ as a better description for the equation of state. We propose to call $G(v,T)$ a generalized Grüneisen parameter. The LJD and MC results will be discussed below. Both approaches also confirm the expected behavior of the specific heat, C_v , in going from the gaseous region to the region of solid densities. This, too, will be discussed.

2. THE LENNARD-JONES DEVONSHIRE EQUATION OF STATE

Lennard-Jones and Devonshire⁴ devised a cell model to describe the equation of state of a liquid (or solid?) in the region from critical density to very high density. In this model the pressure arises from two terms; one due to the mean spacing of molecules in a face-centered cubic configuration, $p_0(v)$, and one due to the motion of each molecule in a cell bounded by its near neighbors considered to be at rest, $p_T + p_1$.

A reexamination by the present author of the excess potential experienced by a molecule in a cell shows that for v/v_0 about 1 or slightly less than 1 ($v_0 = N r_0^3 \sqrt{2}/2$ for an FCC configuration; r_0 is the molecular separation at the minimum of a pair potential), the extra potential due to displacement, r , of the central molecule is approximately quadratic in r when the displacement is small. This implies near to harmonic motions in the system and therefore the LJD equations should be representative of a nearly harmonic solid at these densities if the temperature is low. As the density or displacement increases the excess potential becomes less harmonic; the Grüneisen parameter should then be that of an anharmonic solid. G will here be less than the values G_0 computed from the potential function in the zero degree limit. When v/v_0 is about 1.2 and greater the excess potential begins to look more like a square-well. In this volume region the equation of state should appear to be more like that of a dense gas. At very large volumes the LJD solution is forced to give the ideal gas limit. Thus an examination of $G(v,T)$ for the LJD model should not only show the solid-like behavior at high density and a gas-like behavior at low but also give information about the temperature dependence of the Grüneisen parameter.

The original LJD equations with refinements to include second and third nearest neighbors for the excess potential have been tabulated by Wentorf, et al⁵ from computer runs with the LJ 6-12 pair potential. The resulting equation of state is of the form of Eq. (5) with

$$G(v,T) = 1 + (43\epsilon_m/kT) \cdot A \quad (9)$$

and

$$p_0 v/NkT = (12\epsilon_m/kT) \cdot B \quad (10)$$

where ϵ_m is the magnitude of the pair potential minimum. In the above

$$A = (v_0/v)^4 g_4/G_1 - (v_0/v)^2 g_m/G_1 \quad (11)$$

and

$$B = 2.0219 (v_0/v)^4 - 2.4090 (v_0/v)^2 \quad (12)$$

(The coefficients in Eq. (12) would be 2 if only nearest neighbors were taken into consideration; here all pair potentials are considered for computing the average potential.) The g 's and G_1 are functions of T as well as v . They are represented by integrals which cannot be expressed analytically, hence they were tabulated. Two tables are of interest to us here; (a) the compressibility factor, $P(v,T)$ and (b) the specific heat of gas imperfection vs reduced temperature $\theta = kT/\epsilon_m$ and reduced volume v/v_0 . The table of $C_v - C_v(\text{ideal})$ shows the specific heat to increase from the ideal gas value $C_{v1} = 3Nk/2$ to very nearly the classical solid value $3Nk$ at high density and moderate temperature. The other table is not so explicitly clear. $P(v,T)$ ranges from 1 at low density, high temperature to negative values at $v/v_0 > 1$ at low temperature and then to extremely high values for $v/v_0 < 1$ at low temperatures (see Table 1a). The significant consequences of the theory regarding equation of state are completely obscured by not filtering out the volume dependent pressure, P_0 .

Fortunately $G(v,T)$ can be easily computed from Eq's (5), (10), and (11) since B in Eq. (12) is a simple analytic expression. This has been done for the values of $P(v,T)$ shown in Table 1a. The results are shown in Table 1b and in Figure 1. Two consequences of the LJD theory are immediately apparent from Figure 1. First, at low temperature $G(v,T)$ has a maximum which shifts toward lower volume as the temperature increases. Second, the function is greater than 1 over a wide temperature range and the isotherms show an essentially monotone shift to the left as θ increases. It appears that isotherms could be readily fit by an analytic function to connect the LJD equation to a complete analytic form to any desired degree of precision. In addition, the use of p_0 and G to describe the equation of state provides greater flexibility for a closer examination of the effect of changes in the form of the potential function on the equation of state.

3. THE MONTE CARLO EQUATION OF STATE

The Monte Carlo method for an equation of state due to Metropolis⁸, et al has been evaluated by Wood and Parker⁹ for the LJ 6-12 potential. In the paper by Fickett⁷ graphs of $\Delta(E'/RT)$ and $\Delta(pv/RT-1)$ are presented⁹ to show the consequences of the numerical calculations. Also shown are some results for the LJD free volume theory.¹⁰ We note that $\Delta(pv/RT)$ is, in fact, $G(v,T) = (p-p_0)v/RT$.⁹ With this interpretation it becomes clear that Fickett and Wood⁷ recognized the merit of subtracting out the volume dependent pressure. Their results for E'/RT (the excess energy due to specific heat being a function of volume as well as temperature) indicates for MC that at $v/v_0 < 1$ an additional specific heat of about $3Nk/2$ is added to the ideal gas value as required in going from an ideal gas to a classical solid. The $G(v,T)$ behavior for MC, Figure 2, is qualitatively similar to that of LJD. A much sharper maximum (essentially a peak)

is seen for the isotherms and the curves are flatter to the left of this break. The $\theta = 2.74$ isotherm was not fit by a curve in Reference 7, but the sharp peak which is indicated is probably real. This behavior was predicted near the melting point by Lennard-Jones and Devonshire¹¹ in their theory of melting.

The Monte Carlo method appears to be a powerful tool for establishing the equation of state in the high density regime. What we have learned from its use with the LJ potential can serve as a guide for generating the thermal $G(v,T)$ term for other potentials as well. It appears to give a far better description of the properties of a molecular aggregate than does the cell model of Lennard-Jones and Devonshire. It would now be extremely valuable to extend the MC computation to use other potential functions, e.g. the Morse potential or the modified Buckingham (Expo-6) potential which are believed to be more accurate descriptions for non-ionic non-metallic substances at high density. In the absence of this knowledge, we attempt in the next section to formulate an analytic equation of state based on the preceding work of Fickett and Wood.

4. AN EMPIRICAL FIT TO THE MONTE CARLO EQUATION OF STATE

Of the two examples given, the MC method appears to be the more accurate. The model in contrast to the cell model is truly solid-like in the dense region and gas- or liquid-like in the less dense region. The behavior of $G(v,T)$ suggests that the high density branch can be represented by a generalized Grüneisen parameter for a quasi-harmonic solid while the liquid-gas branch at lower densities might be represented by a virial expansion using a temperature dependent covolume parameter. (The curves on the right of Figure 2 show the volume to vary approximately as $1/\rho^{1/4}$ for any constant value of $G(v,\theta)$.) We propose to represent the liquid-gas branch by a modification of the hard sphere virial expansion in v by replacing the constant covolume b with a temperature dependent covolume $b(T)$ or $b(\theta)$ varying as $1/\rho^{1/4}$. This temperature dependence is in agreement with the behavior in the second virial coefficient result of Lennard-Jones^{12,13}.

The virial equation (Eq. 3.6-1 of Reference 1) is used to define $G(v,T)$ as

$$G(v,T) = 1 + B(T)/v + C(T)/v^2 + D(T)/v^3 + \dots \quad (13)$$

in which B , C , and D , etc., are related to the repulsive part of the second virial coefficient as formulated in Reference 12 (see Appendix A, Eq. (A-4)). We assume³

$$\begin{aligned} B(T) &= b(T) = b \\ C(T) &= .625 b^2 \\ D(T) &= .2869 b^3 \\ E(T) &= .115 b^4 \end{aligned} \quad (14)$$

where $b(T) = C/\sqrt{2} \Gamma(3/4) B_0 / A^{1/4} = 1.7330 C B_0 / A^{1/4}$ for the LJ (6-12) potential. The equation of state for the moderate density region ($A \geq 2.7$) is completed by adding on the volume dependent pressure term as given in Eq. (12). The attractive part of the second virial coefficient as approximated in Eq. (A-4) is omitted. The complete equation written in terms of A is:

$$pV = Nc_m A G(v, A) + 12Nc_m [2.0219 (v_0/v)^4 - 2.4090 (v_0/v)^2] , \quad (15)$$

$$G(v, \theta) = 1 + x + .625x^2 + .2869x^3 + .115x^4 ; \quad (16)$$

where

$$x = b(T)/v . \quad (17)$$

For comparison with Figure 2 it is necessary to express B_0 in terms of v_0 . From the definitions $v_0 = N/\sqrt{2} r_0^3/2$ and $B_0 = 2\pi N\sigma_0^3/3$, and from the relation $(\sigma_0/r_0)^3 = \sqrt{2}$ we find $B_0 = 2\pi v_0/3$. Good fit of Eq. (16) to the MC data is found when $C = 0.91$ provided the fifth virial coefficient $E(T)$ is zero, Figure 3. When the 5 virial coefficients are used the function is too stiff, i.e. it rises too rapidly with decreasing v/v_0 . It must be emphasized that Eq. (15) is limited to the fluid region and ceases to apply when the solid branch is reached. For the solid region we propose a volume dependent Grüneisen term of the form

$$G_s(v) = g_0 + g_1 (v/v_0)^3 . \quad (18)$$

The MC results suggest $g_0 = 6.3$, $g_1 = 3$. $G_s(v)$, with these constants is shown in Figure 3. Eq. (18) with these constants approximates 0.9 times the Dugdale-MacDonald formula result for a nearest neighbor calculation of the Grüneisen parameter. In defining the equation of state the lesser of the values $G_s(v)$ or $G(v, \theta)$ is to be used. The equation of state is in fact two equations. There will be an obvious discontinuity in the partial derivative $(\partial p/\partial v)_T$ at the volume at which $G(v, T) = G_s(v)$. Through this volume region there will be a first or second order transition and free energy arguments can be used to establish the equilibrium conditions.

5. DISCUSSION

The utility of separating variables and thereby defining a thermal pressure term for a general equation of state should be quite clear from the examples cited. By so doing it becomes possible to examine the results of complex statistical mechanical calculations and arrive at an understanding of their physical implication much more clearly. Examination of $G(v, T)$ for the LJD cell model suggests that the model is more descriptive of an anharmonic solid than of a fluid for $v/v_0 > 1$. By comparison with the Monte Carlo method the effect of imposing long range order in a region where such order does not exist becomes readily apparent. This point is not revealed when one examines and compares $F(v, T)$ for the two methods.

The logical separation of variables from the theoretical calculations simplifies the syntheses of empirical equations. One which can be readily handled is given. The empirical relations so derived can be more easily used, checked, and modified to reproduce experimental thermodynamic properties. Comparison of the LJ second virial coefficient results with MC and LJ¹⁰ indicates that $p_0(v)$ is incorrectly defined by the mean lattice positions of molecules when the volume is large. A more precise statistical description is needed to bridge $p_0(v)$ in the volume region from the normal solid to the ideal gas.

At this point a comment on the hard sphere molecule and the virial coefficients for it appear to be in order. Data of Alder and Wainwright¹⁴ on MC calculations for the hard sphere molecule has been plotted in Figure 2. To plot these curves the hard sphere diameter has been taken to be σ_0 , the value of r on the LJ potential at which the potential is zero [v_0 (Alder) = v_0 (this work) $\sqrt{2}/2$]. It is interesting to note that the computer runs show two distinct branches, solid and fluid. The order-disorder transition is seen to occur, surprisingly, at just about where it would be expected for the normal melting of real molecular solids. By comparison with the MC results for an LJ potential one sees that the contribution of the potential function is to determine the transition volume as a function of temperature. (The potential function also supplies the internal pressure term which is necessary to obtain a normal melting point.) For the hard sphere molecule the transition is independent of temperature since G (or F) is a function of volume only. Aside from its use for transition observance, the solid branch is of no great significance. At volumes less than the transition volume G , in real molecular systems, is dominated by an approach to harmonic oscillation; the extremely large values of $F(v)$ of the rigid sphere cease to describe the equation of state behavior of real molecules correctly.

A further conclusion which can be drawn from the solid-fluid transition in the MC computations is that the transition is determined by the effective size of the molecule as a function of temperature. In this regard the recent theory of Kraut and Kennedy¹⁵ on melting temperature vs volume would appear to be amenable to theoretical treatment in terms of the covolume change with temperature. It is suggested that by an inverse relation information about the potential function could be obtained at high density from experimental data on melting point as a function of volume.

One last point; in the case of rapid compression, as in a shock wave in a liquid or disordered solid, or in a detonation of a solid molecule, it is very likely that the solid branch for $G(v,T)$ will differ from the MC results of Fickett and Wood because of disorder. One might expect the generalized Grüneisen parameter for a disordered solid to differ from the results reported. But the difference is unlikely to be predicted by an extension of the fluid branch as the volume decreases. The exact behavior is a problem yet to be solved. A discussion on the application of the ideas presented

here to the problem of defining the equation of state for dense product states of condensed explosives was presented at the 12th Symposium on Combustion, Poitiers, France in July 1968.¹⁶

6. ACKNOWLEDGEMENTS

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$$p_L v/RT = 24[1.011(r/r^*)^{-12} - 1.2045(r/r^*)^{-6}]/\theta, \quad p_L \text{ is the lattice pressure.}$$

Then $\Delta(pv/RT-1) = G-1$ as defined here.

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APPENDIX A

Lennard-Jones^{1,2,13} has given a statistical mechanic solution for the second virial coefficient based on a bireciprocal potential. His equations¹³ may be written as

$$B(\theta) = \frac{2}{3} \pi N r_0^3 (m/n)^{3/(n-m)} f(\theta) \quad (A-1)$$

$$f(\theta) = F(y) = y^{3/(n-m)} \left[\Gamma\left(\frac{n-3}{n}\right) - \sum_{\tau=1}^{\infty} 3\Gamma\left(\frac{\tau m-3}{\tau}\right) y^{\tau/\tau!n} \right] \quad (A-2)$$

and

$$y = (m/n)^{-1/n} \left[\frac{n}{(n-m)\theta} \right]^{(n-m)/n} \quad (A-3)$$

where m and n are the attractive and repulsive exponents and θ is the reduced temperature kT/ϵ_m . $\Gamma(x)$ represents the gamma function of the argument x and r_0 is the molecular separation at equilibrium. It is immediately apparent that the coefficient of $f(\theta)$ is just $\frac{2}{3} N k \sigma_0^3 = B_0$ so that Eq. (A-2) for $F(y)$ is just $B(\theta)/B_0$. For $m = 6$, $n = 12$, we find that the first term in B (from Eq. (A-2) and (A-3)) varies as $\theta^{-1/4}$. To establish the behavior of the second term, Eq. (A-2) was solved for the two terms in $B(\theta)/B_0$ using a high speed computer and a subroutine for $\Gamma(x)$ ¹⁷. Twenty terms were used in the summation. The result for $B(\theta)/B_0$, Table A-1, is in complete agreement with the result published in Reference 1.

In Table A-1 $b(\theta)/B_0$ is defined as the first term on the right of Eq. (A-2); $A(\theta)/\theta$ is defined as the second term on the right of Eq. (A-2). Then $A(\theta)$ is just equivalent to van der Waals' a . On examining the table we find that $A(\theta)$ deviates only about $\pm 4\%$ from a constant value 4.3 over the range from the normal boiling point to the critical temperature ($0.8 < \theta < 1.4$). There is a minimum in $A(\theta)$ at $\theta = 1.6$. Above this temperature $A(\theta)$ increases very slowly with temperature. The result indicates that $B(\theta)$ above $\theta = 1.6$ can be represented by an analytically simple function given as

$$B(\theta) = B_0 [1.733/\theta^{1/4} - A(\theta)/\theta] \quad ; \quad A(\theta) = a_1 + a_2 \theta^{1/2} \quad (A-4)$$

With $a_1 = 3.480$, $a_2 = .5282$; $B(\theta)$ is represented to within 1% for $\theta > 10$ and about $\pm .03$ units for $10 > \theta > 1.4$. The fit could be improved in the low temperature region if desired. The Lennard-Jones second virial coefficient thus reduces in essence to that of the van der Waals equation of state with the attractive term $a(\theta) = N \epsilon_m B_0 (a_1 + a_2 \theta^{1/2})$ having a weak dependence on temperature and a repulsive term $b(\theta) = B_0/\theta^{1/4}$. If the term containing a_2 were treated as a correction to $b(\theta)$ then " a " would be a constant.

The second virial coefficient has been solved¹³ for hard sphere molecules with an attractive potential of the form $u = -u_0 (\sigma_0/r)^m$, σ_0 being the molecular diameter. A simple approximation to the result given by Mayer and Mayer¹⁸ for the van der Waals a is

$$a = 3Nbu_0/(m-3) \quad (A-5)$$

Eq. (A-5) can be related to the attractive part of a bireciprocal potential if b is taken as B_0 and u_0 is taken as the attractive energy at the corresponding diameter, σ_0 . For the special case $n = 2m$ it then turns out that $u_0 = 4\epsilon_m$. Thus

$$a = 12N\epsilon_m B_0/(m-3) \quad (A-6)$$

for comparison with $A(\theta)$. For $m = 6$ Eq. (A-6) gives $a/N\epsilon_m B = 4$ which is only a few per cent less than the mean value of $A(\theta)$. We have rerun the LJ second virial coefficient calculations for $m = 4.5$, $n = 9$ to see whether the dependence of $A(\theta)$ on m agrees with the predicted value, 8, of Eq. (A-6). The agreement was positive. $A(\theta)$ for $m = 4.5$ had a minimum value of 8.30 and very nearly double the values shown in Table A-1 over the entire range of θ computed.

There is an alternate approach for replacing the numerical results of Table A-1 by an analytic approximation. The value of $b(\theta)$ is redefined as

$$b(\theta)/B_0 = 1.7330C/\theta^{1/4} \quad (A-7)$$

and $A(\theta)$ is redefined as

$$A(\theta) = \theta[b(\theta) - B(\theta)] \quad (A-8)$$

It was found that if $C = 0.91$, $A(\theta)$ is very nearly a constant with the mean value being 4.1. It has its greatest value of 4.41 at $\theta = 20$ and least values of 3.906, 3.81 at $\theta = 2$ and 80 respectively in the range of θ from 0.8 to 80. This interpretation indicates that over a wide range of θ the attractive term may be represented as a constant to within 10% or less. The diminished covolume parameter defined in Eq. (A-7) is used in Section 4 for the empirical fit to the Monte Carlo results. In that application $A(\theta)$ is assumed to be zero.

We conclude that the LJ second virial coefficient at moderate and high temperatures can be represented by an attractive term and a covolume both mildly temperature dependent. The attractive term is very nearly that of hard sphere molecules with an attractive pair potential. These findings differ with a remark by Lennard-Jones¹³ which says "In the van der Waals molecular model the repulsive and attractive parts of the field are in separate regions of space and it is not surprising that their contributions to the statistical stress should be separable. It is not to be expected that in other models the effects of the repulsive and attractive fields can be so distinguished." It should be mentioned that Lennard-Jones refers to the second virial contribution to the internal pressure as a statistical pressure to distinguish it from p_0 , the derivative of E_0 , which at high density is a much larger contribution to the pressure. We note that the attractive pressure, a/v^2 , in van der Waals equation and as approximated here differs significantly from the attractive contribution to p_0 in Eq. (10). The latter is of the form (const/v^3) .

	$v/v_0 = .565685$.707107	.989949	1.13137	1.41421
.7	215.9	64.01	2.358	-2.642	-3.566
1	154.02	47.1	3.83	.1881	-.8515
2	80.866	27.258	5.123	3.101	1.9919
4	44.01	16.982	5.43	4.11	3.043
7	28.074	12.312	5.259	4.283	3.29
10	21.584	10.373	5.087	4.212	3.305
20	13.735	7.866	4.576	3.92	3.175
50	8.717	5.91	3.905	3.444	2.885
100	6.733	4.902	3.462	3.104	2.657
400	4.476	3.592	2.777	2.543	2.082
	$v/v_0 = 1.69706$	1.81108	2.12132	2.82843	4.24264
.7	-2.535	-2.107	-1.486	-.7382	-.1841
1	-.483	-.3105	-.0547	.2541	.4897
2	1.698	1.624	1.522	1.376	1.176
4	2.565	2.41	2.187	1.874	1.323
7	2.797	2.63	2.385	2.031	1.271
10	2.829	2.666	2.424	2.048	1.219
20	2.76	2.614	2.394	1.901	1.128
50	2.556	2.431	2.178	1.531	1.056
100	2.348	2.188	1.856	1.305	1.029
400	1.661	1.506	1.296	1.085	1.007

TABLE 1b
G(v,T) = (P-P₀) v/NkT vs v/v₀ and Theta

	v/v ₀ = .565685	7.07107	.989949	1.13137	1.41421
.7	6.47121	7.96314	8.40937	8.46725	8.41814
1	7.41984	7.8672	8.06596	7.96457	7.5374
2	7.56592	7.6416	7.24098	6.98924	6.18635
4	7.35996	7.1738	6.48899	6.05412	5.14023
7	7.13112	6.70731	5.36414	5.33392	4.48841
10	6.92398	6.44972	5.5106	4.98965	4.14389
20	6.40499	5.90436	4.7878	4.30882	3.59445
50	5.785	5.12534	3.98972	3.59953	3.05278
100	5.267	4.50967	3.50436	3.18176	2.74089
400	4.1095	3.49392	2.78759	2.56244	2.10297
	v/v ₀ = .169706	1.81108	2.12132	2.82843	4.24264
.7	7.62602	7.26234	5.97986	3.98258	2.0033
1	6.62971	6.24804	5.1714	3.48864	2.02088
2	5.25436	4.90327	4.13505	2.99327	1.94159
4	4.34318	4.04963	3.49353	2.68264	1.7058
7	3.8131	3.56693	3.13159	2.49308	1.48974
10	3.54027	3.32185	2.94661	2.37145	1.37212
20	3.11564	2.94193	2.65531	2.06273	1.20456
50	2.69825	2.56217	2.28252	1.59569	1.08662
100	2.41913	2.25359	1.90826	1.33735	1.04431
400	1.67878	1.5224	1.30907	1.09309	1.01083

TABLE A-1
Lennard-Jones Second Virial Coefficient Values

$\theta = kT/\epsilon_m$	$b(\theta)/B_0$	$A(\theta)/\theta$	$B(\theta)/B_0$	$A(\theta)$
.4	2.17913	15.9777	-13.7985	6.39107
.6	1.236907	8.16704	-6.19798	4.90023
.8	1.83243	5.56666	-3.73423	4.45332
1.	1.733	4.27109	-2.53809	4.27109
1.2	1.65578	3.49174	-1.8395	4.19008
1.4	1.59319	2.96904	-1.37585	4.15665
1.6	1.54088	2.59279	-1.05191	4.14847
1.8	1.49617	2.30821	-.812036	4.15477
2.	1.45727	2.0849	-.627628	4.1698
2.5	1.37821	1.69082	-.312615	4.22705
2.74	1.31698	1.55454	-.207564	4.25945
3.	1.3168	1.43203	-.115236	4.29609
3.5	1.26702	1.24806	.018956	4.36821
4.	1.22542	1.11	.115416	4.44
4.5	1.18986	1.00224	.187617	4.51009
5.	1.15893	.915585	.243343	4.57793
10	.974538	.513663	.460875	5.13663
20	.819486	.294112	.525374	5.88223
30	.740489	.213564	.526926	6.40691
40	.689103	.170528	.518575	6.8211
50	.651713	.143352	.508362	7.16758
60	.622675	.124462	.498213	7.46771
70	.599135	.110484	.488651	7.73387
80	.579464	.099674	.47979	7.9739
90	.56265	.091035	.471615	8.19314
100	.548023	.083954	.46407	8.39536

LIST OF FIGURES

- Figure 1 $G(v,T) = (p-p_0)v/NkT$ from the LJD Free Volume Theory; circles and solid curves from Reference 5, x's and dashed curve from Reference 10. The dimensionless temperatures, $\theta = KT/\epsilon_m$ top to bottom are 0.7, 1, 2, 7, 20, 100, 150, 400. Curves labeled (a) and (b) are G_n for a solid based on the Dugdale and MacDonald formula (Reference D. J. Pastine, Phys. Rev. 138, A767 (1965)). (a) is calculated from the p_0 of Eq. (15); (b) from p_0 based on nearest neighbor interactions.
- Figure 2 $G(v,T)$ from Monte Carlo Method, Reference 7. Values of θ are $\bullet = 100$, $\blacksquare = 20$, $\blacktriangle = 5$, $\blacktriangledown = 2.74$. The dotted curves are for hard sphere molecules. Reference (14) (f) = fluid branch, (s) = solid branch.
- Figure 3 Comparison of Eq's (16) and (18) with Monte Carlo results. Solid curves on right, Eq. (16), curve labeled (a) Eq. (18). MC results labelled as in Figure 2. The dashed curve is the LJD result for $\theta = 20$ for direct comparison.

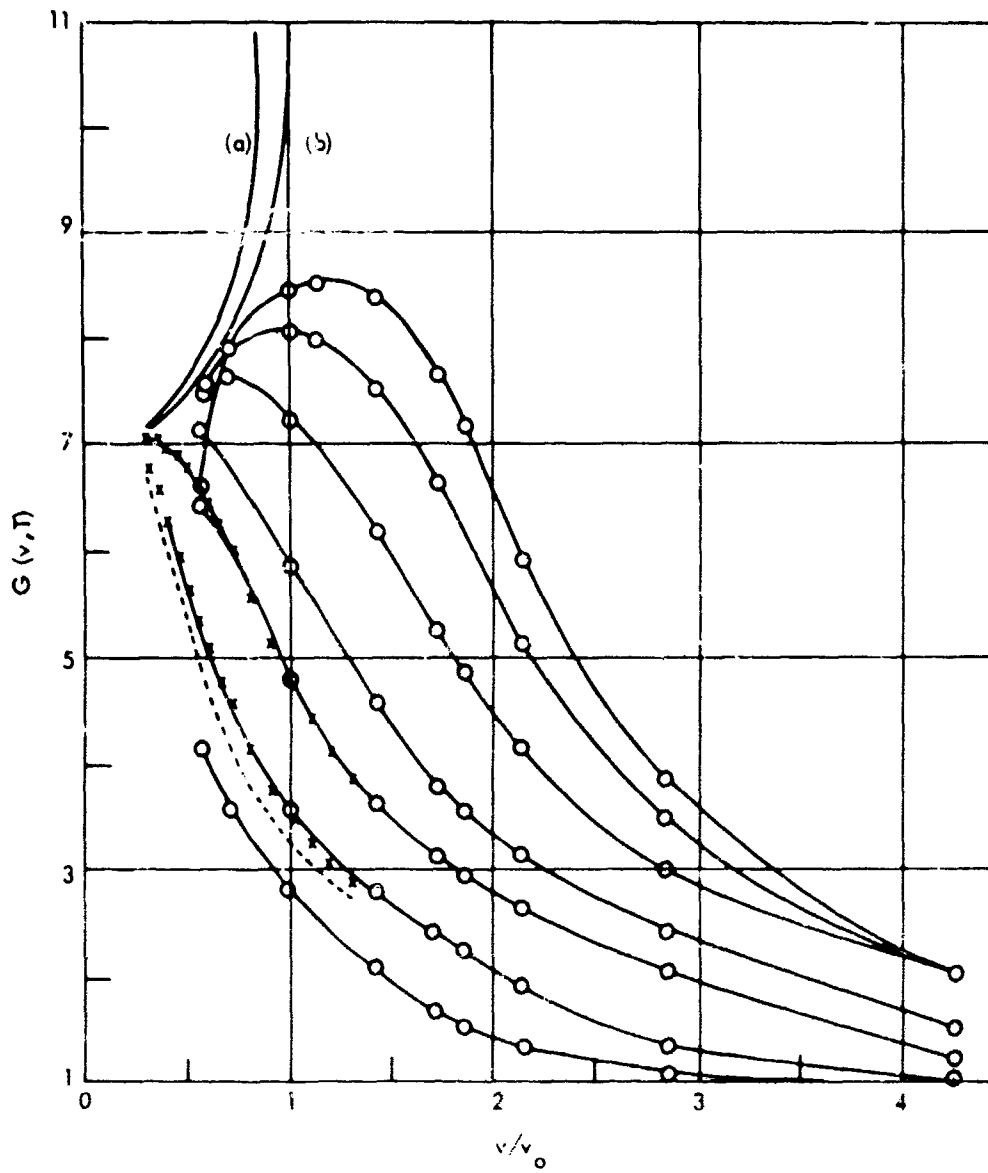


FIG. 1 $G(v, T) = (P - P_0) v / NkT$ FROM LJD THEORY

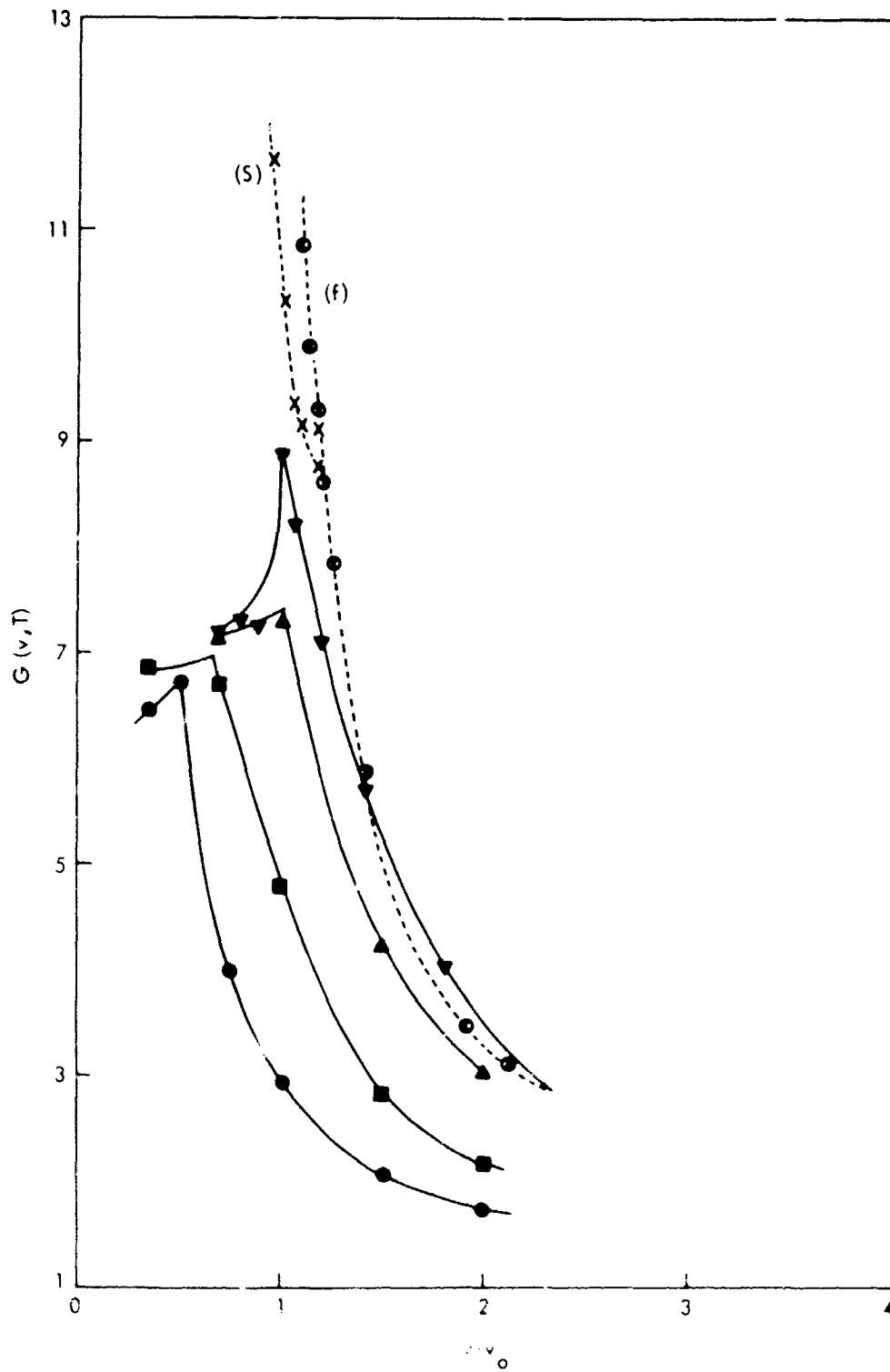


FIG. 2 $G(v, T)$ FROM MONTE CARLO METHOD

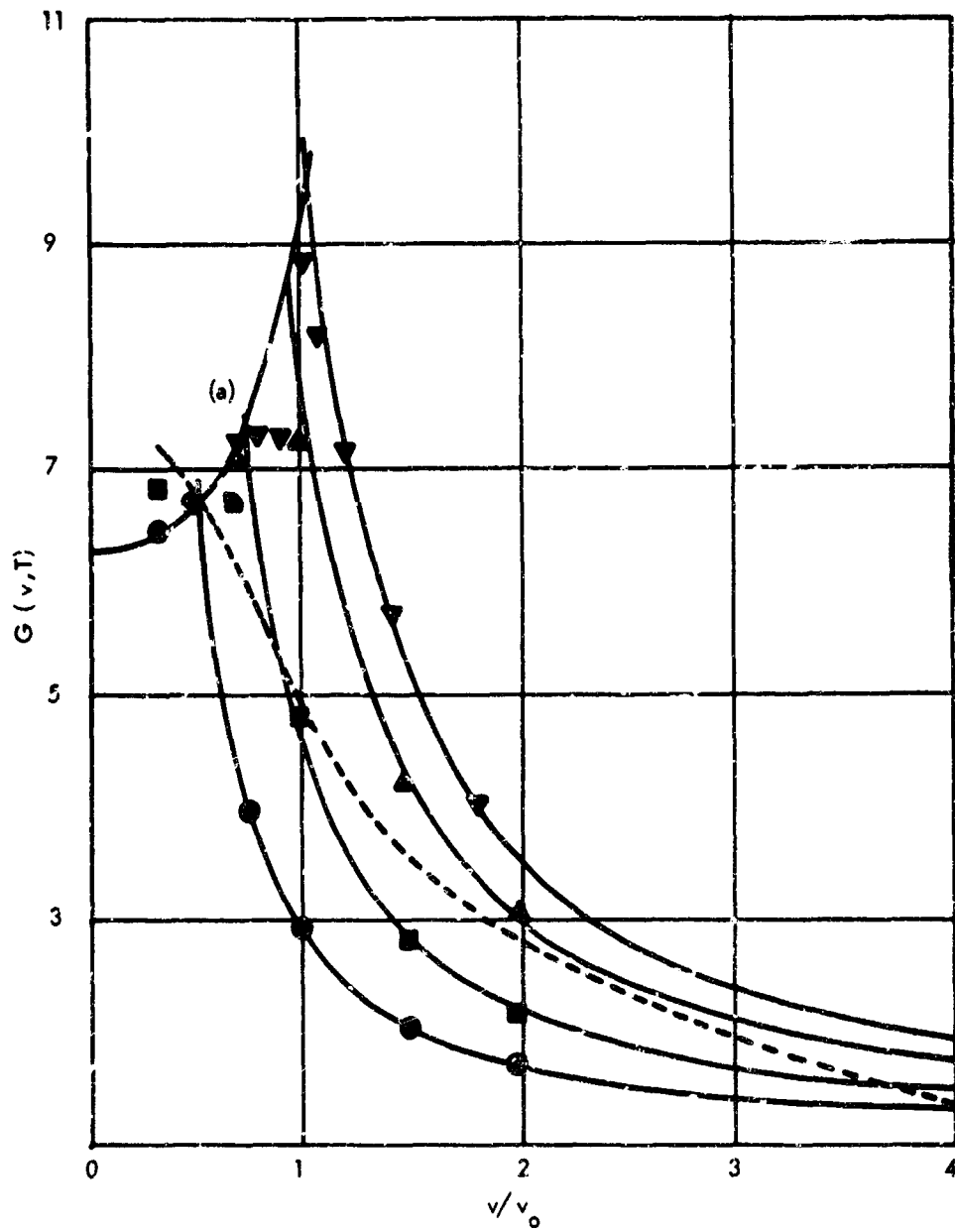


FIG. 3 COMPARISON OF EQUATION (16) AND (17) WITH MONTE CARLO RESULTS

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<p>The work of van der Waals on gases and Mie and Gruneisen on solids produce equations of state of the form $p = G(v,T) NkT/v + p_0(v)$. Many more recent theoretical studies have led to results expressible in the same form. Despite this fact it has been almost a universal fad to describe equations of state through the dimensionless compressibility factor, $F(v,T) = pv/NkT$ instead. This paper shows that much useful information is discarded when the latter form is used. An analysis of p_0 and $G(v,T)$ for the Lennard-Jones Devonshire free volume theory and the equation of state results obtained by the Monte Carlo (molecular dynamics) method has shown that both studies lead to essentially the Mie-Grüneisen equation at high density when the temperature is low enough. At higher temperatures for high density and for all temperatures at lower densities the two theories come close to the usual theories for dense fluids. The functional relations for $G(v,T)$ are sufficiently simple to be replaced by analytic functions to facilitate application of the theories to practical problems. It appears that empirical improvements on the original theories can also be made on the basis of new knowledge about the states under consideration. For illustration an analytic fit to the Monte Carlo result for a Lennard-Jones 6-12 potential is presented. A breakdown of Lennard-Jones result for the second virial coefficient is appended.</p>		

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